69—10

Proceedings of the American Academy of Arts and Sciences.

Vol. 69. No. 10.—November, 1934.

CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 333.

THE APPARATUS AND METHOD USED FOR THE MEASUREMENT OF THE COMPRESSIBILITY OF SEVERAL GASES IN THE RANGE 0° TO 325° C.

By James A. Beattie.

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Received June 23, 1934. Presented October 10, 1934.

1. Introduction.

The experimental investigation of the compressibility of a pure fluid requires the measurement of four quantities—mass, pressure, volume, temperature—and the accurate control of two of these quantities, usually volume and temperature. Keyes[1] has described the apparatus used in the investigation of the compressibility of water; in the present paper are described the disposition of apparatus (many of the individual parts of which are similar to or identical with those of Keyes) and the procedure used in the investigation of the compressibility of the gas phase of several substances.

The temperature range that can be covered is limited at the lower end by the freezing point of mercury under pressure and at the upper end (325° C) by the uncertainties introduced by the presence of appreciable amounts of mercury vapor. The pressure range covered is from 10 to 500 atmospheres. Above 500 atmospheres hysteresis in the dilation of the apparatus begins to appear and affects the accuracy of the volume measurements. An advantage of the method is that the effect of temperature and pressure on the volume measuring system is experimentally determined.

The individual units for the determination of mass, pressure, volume, and temperature have been carefully checked over a period of years. Pressures are expressed in terms of the vapor pressure of carbon dioxide at 0° C (34.401 normal atmospheres), the volumes of the gas at any temperature are expressed in terms of the specific volume of liquid mercury at that temperature and one atmosphere, temperatures are expressed on the international platinum resistance thermometer scale.

2. The Apparatus.

The general disposition of the apparatus is shown in Fig. 1. A weighed portion of the gas is contained in the bomb *F* of about 200 cc.

[1] F. G. Keyes, Proc. Am. Acad. Arts and Sci., **68**, 505 (1933).

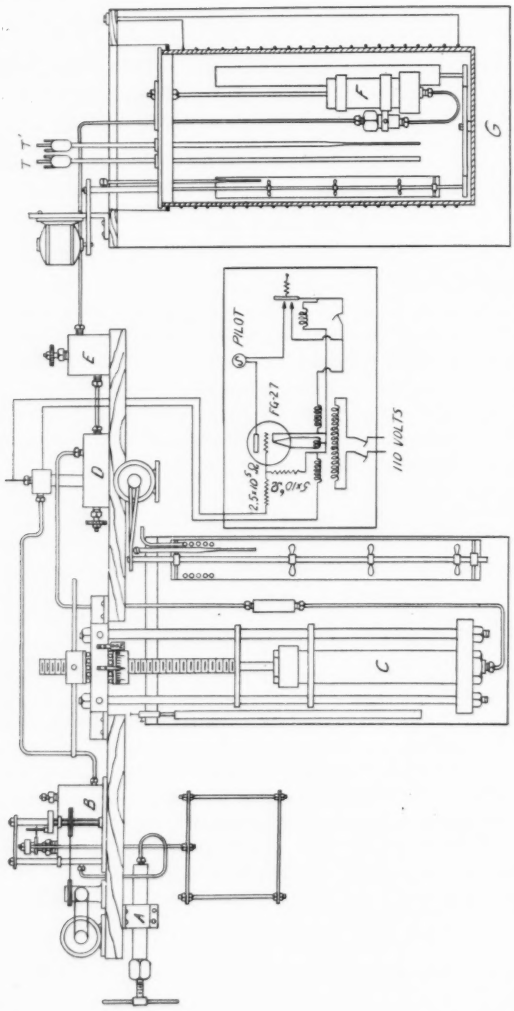

FIGURE 1. Sketch of the Compressibility Apparatus.

capacity. The volume of the gas space is controlled and measured by the introduction or removal of known volumes of mercury by means of the mercury compressor C of about 210 cc. displacement, which is connected to the bomb by steel capillaries. The temperature of the gas is controlled by the thermostat G and the control platinum resistance thermometer T', and measured on the platinum resistance thermometer T. The pressure is measured on the gauge B, being transmitted by oil from the tip of the insulated needle in the riser-block D to the gauge.

Measurement of Pressure. The pressure gauge, Fig. 2[2], is of the Amagat dead-weight type, and is a development from an earlier design of Keyes.[3] The cylinder F carrying the piston C is held in the

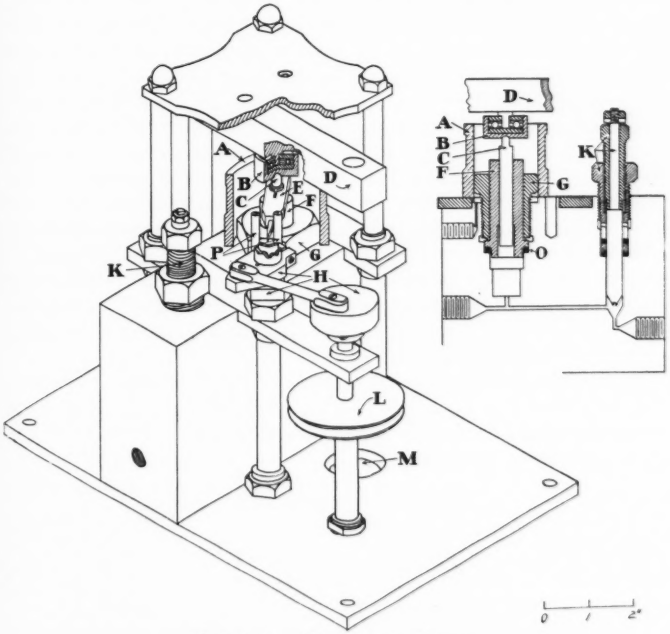

FIGURE 2. The Pressure Gauge

[2] This is a reproduction of Fig. 4 of Keyes, reference 1.

[3] F. G. Keyes and R. B. Brownlee, "The Thermodynamic Properties of Ammonia." New York: John Wiley and Sons, 1916.

block by a nut G that presses the bottom of a flange on the cylinder against an aluminum gasket O. Several piston and cylinder combinations of different effective areas may be used interchangeably in the same block, since the cylinders all have the same external dimensions. The weights used to balance the thrust due to the pressure are placed on a scale pan (see Fig. 1) suspended from the cross-arm D that rests on a ball-bearing B at the top of the piston. The piston is rotated backwards and forwards 30 times a minute through an angle of 60° by means of two rollers P that alternately engage the clip E fastened to the piston. At the end of each stroke there is a short time during which the clip E is not in contact with either of the rollers P; and it has been found that in this interval the piston is not in electrical contact with the cylinder and hence is floating freely in oil. The free vertical travel of the piston is about 1 cm. The oil that leaks out around the piston is replaced from an oil injector A, Fig. 1.

The pistons and cylinders are hardened, ground, and lapped, and are manufactured by Pratt and Whitney Company. The requirements[4] of a proper piston and cylinder combination are: (1) the maximum variation in diameter of the piston throughout its entire length should be 0.0001 cm. or less; (2) when lubricated with oil and pushed back and forth through the cylinder several times, the piston should slide through the cylinder under a force of 100 grams with a velocity of about 1 cm. per second without sticking in any position; and (3) under a load of 250 kilograms (the maximum used) the piston should sink, due to oil leakage between piston and cylinder, not faster than 1 cm. in 20 minutes. The oil used for the last two tests should have a viscosity of about 50 centipoise at 38° C.

The relation between the constant C' of a piston-cylinder combination in normal mm. of mercury (1 mm. = 1/760 normal atmospheres) per gram-weight (1 gram-weight = g dynes) and the effective diameter d_e in centimeters is

$$C'd_e^2 = \frac{40\,g}{\pi\rho g_s} = 0.000955008\,g, \tag{1}$$

where ρ is the standard density of mercury (13.5951 gm. per cm.^{3}), g the value of gravity at the place where the gauge is used, and g_s standard gravity (980.665 dynes per gram).

The effective diameter of a proper piston-cylinder combination calculated from the formula

$$Cd_e^2 = 0.000955008\,g, \tag{2}$$

[4] J. A. Beattie and O. C. Bridgeman, Ann. der Physik, [5] **12**, 827 (1932).

where C is the gauge constant in normal mm. of mercury per gram of brass-in-air (1 gram of brass-in-air = $(1 - 0.0012/8.4)$ g dynes = 0.99986 g dynes), is very closely 0.00025 cm. greater than the actual diameter d of the piston. The constant C computed from the relation

$$C = \frac{0.000955008\ g}{(d + 0.00025)^2} \tag{3}$$

is usually within $\pm$ 0.03% of the actual constant.

The following considerations should be mentioned:

1. The gauge constant C is determined by calibration against the vapor pressure of carbon dioxide at 0° C. as described by Bridgeman.[5] His value of this vapor pressure—26144.7 normal millimeters or 34.401 normal atmospheres—is used. The calibration can be made with a precision of 0.004%.

2. For both the calibration and the subsequent use of the gauge, the weight of the scale pan, cross-arm, ball-bearing, piston, clip, and the "weights" are determined by weighings in air against brass standards and are not corrected for air buoyancy. This correction is unnecessary since the maximum effect of *variations* in air buoyancy is less than one part in 100,000.

3. It has been found[6] that the variation of the gauge constant with pressure does not exceed 0.02% in the range from 10 to 500 atmospheres.

4. The variation of the gauge constant with temperature due to thermal expansion of the steel is given by the relation

$$C_{t_1} = C_{t_2}[1 + 2.2 \times 10^{-5}(t_2 - t_1)], \tag{4}$$

where $t_2 - t_1$ is expressed in Centigrade degrees.

5. The gauge constant increases (*i. e.* the effective area decreases) with time,[4] this increase being approximately 0.01% per year for a new piston-cylinder combination.

6. In the correction for oil-level difference, the level in the gauge is taken at the bottom of the piston. If the level were taken at any other place on the piston a correction for the buoyant effect of the oil must be applied which exactly compensates for this difference.

The riser-block D, Fig. 1, for the detection of pressure equilibrium[3] consists essentially of a steel tube of 3/16 inch bore into the top of which projects an electrically insulated steel needle.[1] Above the tip

[5] O. C. Bridgeman, J. Am. Chem. Soc., **49**, 1174 (1927).

[6] F. G. Keyes and J. Dewey, J. Opt. Soc. Am., **14**, 491 (1927); J. A. Beattie and W. L. Edel, Ann. der Physik, [5] **11**, 633 (1931).

of the needle is the oil which transmits the pressure to the gauge and below is the mercury of the volume control system. When there is too little weight on the scale pan the mercury surface rises and makes electrical contact in the grid circuit of a thyratron, when there is too much weight the mercury surface falls and electrical contact is broken (see Fig. 1). A pilot light in the anode circuit of the thyratron indicates when contact is made or broken. Thus the leakage of oil around the piston of the pressure gauge, if not too great, has no effect on the detection of pressure equilibrium. When other things are constant, a change in weight of 0.001% to 0.002% on the scale pan produces a positive effect within 1 to 2 minutes.

Control and Measurement of Temperature. The thermostat *G*, Fig. 1, has been described in detail elsewhere.[7] The outer can is of galvanized iron and is 39 inches deep by 29 inches in diameter. The inner vessel is made by welding a bottom into a 28 inch length of wrought iron pipe 14 inches in diameter and 5/16 inch wall thickness. It rests on fire brick and is surrounded by 85% magnesia. It is wound with three 50-foot 20-ohm heaters through which sufficient current is passed to keep the temperature 2° to 3° below the desired operating value.

The stirrers are suspended between two plates one of which rests on the bottom of the inner vessel and the other turned to a tight fit to the top of the inner vessel. Three shafts each carrying three propeller-type stirrers and each enclosed in a steel tube 2-3/4 inches in diameter are spaced 120° apart and run in bearings at the top and bottom. The shafts are geared together and rotated at about 1700 revolutions per minute. The bomb and platinum resistance thermometers are introduced through tight-fitting split heads. For temperatures to 125° C, Socony Mineral Seal oil (a high grade kerosene) is used as the bath fluid; for temperatures above 125° C, Socony Vacuum S/V Valrex oil A. mineral (a heavy cylinder lubricating mineral oil) is used. At 325° C. this oil decomposes, but not rapidly enough to cause trouble.

In the top of each stirrer tube is inserted a flat-type heater of about 30 ohms resistance. The three heaters are connected in series and are used for the final adjustment and the regulation of temperature.

The method of regulation is a development of methods previously used.[8] A flat-type platinum resistance thermometer is placed in the

[7] J. A. Beattie, Rev. Sci. Instr., **2,** 458 (1931).

[8] J. R. Roebuck, Proc. Am. Acad. Arts and Sci., **60,** 537 (1925); L. B. Smith, Mech. Eng., **48,** 153 (1926); J. A. Beattie and D. D. Jacobus, J. Phys. Chem., **34,** 1254 (1930); F. G. Keyes, Proc. Am. Acad. Arts and Sci., **68,** 505 (1933).

bath and its resistance balanced on a Wheatstone bridge which is connected to a galvanometer in the usual manner. A beam of light is reflected from the galvanometer mirror to a selenium cell contained in a dark box about 20 feet away. The variation in resistance of the selenium cell is used to control the current input to the internal heaters by means of the phase-shifting thyratron circuit, Fig. 3, proposed by Hull.[9] As the temperature of the thermostat drops the spot of light from the galvanometer moves so as to illuminate a larger area of the selenium cell, thus decreasing its resistance, whereby the current in the anode circuit (which contains the internal heaters) increases; as the temperature of the thermostat rises the spot of light moves so as to illuminate a smaller area of the selenium cell and the heating current decreases. At about 0.5 amperes regulating

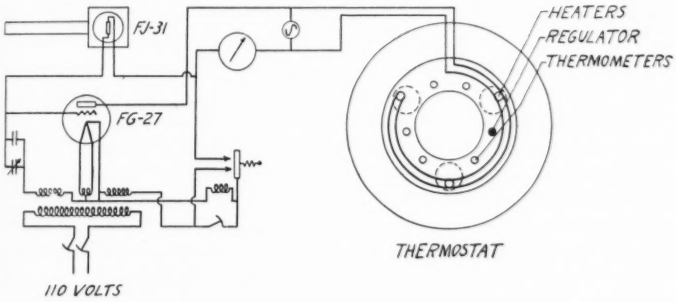

FIGURE 3. The Temperature Regulating Circuit.

current the variation due to the operation of the circuit is about $\pm$ 0.05 amperes. For best results the spot of light should not be a sharp image of the lamp filament, but rather broad. The sensitivity of the regulation depends on the correct capacity balance, which must be determined for each installation. A fixed condenser is used for the greater part of the capacity and a 0.00035 mf. variable radio condenser for the fine adjustment. In this manner thermostats have been regulated at temperatures from 25° to 325° C. to $\pm$ 0.0005° C. for several hours, and regulation to $\pm$ 0.001° C. can be obtained for longer periods without difficulty.

Temperatures are measured by means of strain-free platinum

[9] A. W. Hull, Gen. Elec. Review, **32**, 390 (1929).

resistance thermometers of the mica-cross type.[10] The thermometers are calibrated at the ice point (0° C), steam point (100° C), and sulfur boiling point (444.6° C). The hypsometers, which will be described in a later paper, are so arranged that the pressure at which boiling occurs can be held constant to ± 0.01 mm. and at one normal atmosphere. Interpolation is made by use of the Callendar formula:

$$t = \frac{R_t - R_o}{\alpha R_o} + \delta \frac{t}{100}\left(\frac{t}{100} - 1\right), \tag{5}$$

where t is Centigrade temperature on the international platinum resistance thermometer scale; R_t and R_o are the electrical resistances of the given thermometer at $t°$ and 0° C, respectively; and α and δ are two constants determined by the calibration at the steam and sulfur boiling points, respectively. For the calculation of the resistance R_t corresponding to a desired temperature $t°$ C, the equation is written:

$$R_t = R_o\left\{1 + \alpha\left[t - \delta\frac{t}{100}\left(\frac{t}{100} - 1\right)\right]\right\}. \tag{6}$$

Control and Measurement of Volume. The volume of the gas in the bomb is controlled and measured by the addition or removal of mercury by means of the mercury compressor *C*, Fig. 1. It consists of a cold rolled steel cylinder 1 1/16 inch inside diameter into which fits a piston of 1 inch drill rod, the packing gland at the top being made tight by cloth dipped in ceresine wax which is confined between hard rubber rings and compressed between hardened steel rings by a cap nut. The bottom of the cylinder is securely anchored to the bottom of the heavy yoke that supports and aligns the piston and cylinder. The piston is pinned to a 1½ inch rod threaded with an 18 pitch buttress thread, which passes through a Tobin bronze nut. This nut passes through the top member of the yoke and has roller bearings on its upper and lower bearing surface. Full turns of the nut are registered on a revolution counter and thousandths of turns can be estimated from a calibrated dial on the nut. The compressor is thermostated at 30° C ± 0.002°. A steel capillary (1/8 inch outside diameter, 1/32 inch bore) runs from the bottom of the cylinder to the riser block and thence to the bomb containing the gas under investigation.

The piston is 1 inch in diameter and has a travel of 16 3/8 inches corresponding to 294 turns of the nut and to about 210 cc. of mercury.

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[10] J. A. Beattie, D. D. Jacobus, and J. M. Gaines, Jr., Proc. Am. Acad. Arts and Sci., **66**, 167 (1930).

For the calibration of the compressor a very fine glass capillary is cemented to the upper end of the steel capillary and the mercury forced out by each ten turns of the nut collected in weighing bottles. The nut is first turned back to -1 turns then rotated forward to 0 turns; after a wait of ten minutes the first weighing bottle is put under the tip and the nut rotated forward to 10 turns; after a wait of ten minutes the second weighing bottle is put under the tip and the nut turned to 20 turns, etc. The cumulative volume of mercury V forced out at 30° and 1 atmosphere is expressed by the equation:

$$V = aC + \delta C, \tag{7}$$

where a is a constant and C the reading of the compressor in turns and fractions of a turn. The deviation δC from linearity is plotted against the volume V, the greatest deviation being 0.011 turns (0.008 cc). Several calibrations of the compressor and the subsequent use of it indicate that the readings are significant to 0.005 turns, or 0.004 cubic centimeters.

It will be noticed that there are two stopcocks in the mercury line, one in the riser block and one between the riser block and the bomb. They are of the type described by Keyes,[1] except that the stem is ¼ inches in diameter and the handle is fitted with a calibrated dial. The stopcocks are opened exactly the same amount each time so that no volume errors are introduced.

The Bombs. The all-steel bomb, *A*, Fig. 4, used for substances whose vapor pressure is above 15 atmospheres at 30° C, is made of chrome-vanadium steel and has a volume of about 200 cc. The closure is made on a soft steel gasket (1/8 inch wide and 1/16 inch thick) made from a piece of cold rolled steel in which the carbon has been precipitated by heat treatment. The gasket is confined in a ring-shaped depression in the bottom of the bomb by a ridge on the cover, the bottom of the depression and the top of the ridge containing two slight grooves to hinder flowing of the gasket. The cap nut is tightened with an eight-foot wrench. From the bottom of the bomb a capillary leads to a cone connection *bc*, similar to that described by Keyes,[1] and thence to the riser-block. For the evacuation or filling of the bomb a gold washer 0.01 inches thick is bent up slightly in the middle, placed in the recess in the cone *c*, the drilled screw inserted, and *c* joined to the connection *a*. After the evacuation or filling is completed the drilled screw is tightened on the gold washer by means of a screw-driver that passes through a packed gland in the top of *a*. The connection *a* is then replaced by *b* and the gold washer subsequently

punctured by the application of several hundred atmospheres pressure of mercury.

The glass-lined bomb *B*, Fig. 4, is used for substances whose vapor pressure is less than 15 atmospheres at 30° C. The glass liner is evacuated or filled through a very fine capillary, the substance frozen in the bottom by immersion in liquid air, and the capillary sealed off, bent, and scratched with a file very close to the end of the bore. The liner is then placed in the chrome-vanadium steel case, the latter closed in the usual manner, and connected to the riser-block. The

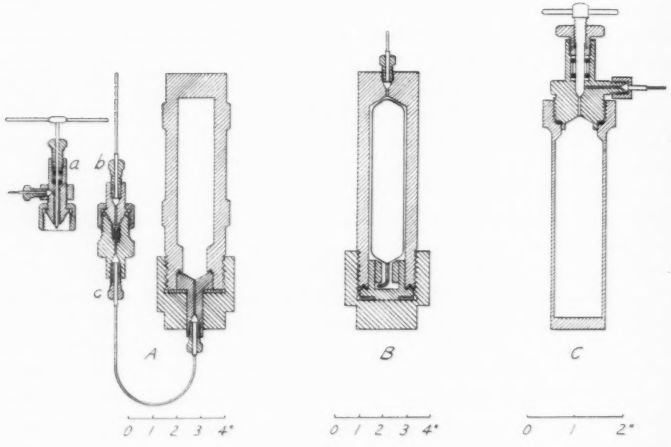

FIGURE 4. A, the All-Steel Bomb; B, the Glass-Lined Bomb; C, the Weighing Bomb.

bomb is placed on its side in the thermostat at 30° C, evacuated, mercury run in, and the bomb then turned upright. The liner floats up and the tip breaks at the file mark.

Weighing Bombs. The substance to be investigated is weighed in the stainless steel bomb *C*, Fig. 4. A second of almost identical outside dimensions is used as a tare to reduce air-buoyancy corrections to a minimum. The bomb is evacuated, rinsed out with the substance several times, approximately the desired mass of the substance introduced, and weighed against the tare. The substance is then transferred to the compressibility bomb (the latter being cooled in liquid

air), the gold washer tightened or the glass liner sealed off, as the case may be, the residual pressure read on a McLeod gauge, and the weighing bomb closed and weighed. For all weighing both bombs are closed, vacuum corrections being applied for the difference in external volume and for the weights.

In some cases the substance to be investigated has been weighed directly in the glass liner against a tare of as nearly as possible the same weight and outside dimension. Both the liner and the tare were cemented to a vacuum line, evacuated, filled with laboratory air, and the relative weight determined. The substance was then introduced into the liner, frozen in the bottom, and the liner sealed off; the tare was evacuated and sealed off; and the relative weight determined. Proper vacuum corrections were applied in both weighings. This method has not been used since the construction of the steel weighing-bombs.

3. The Blank Run.

A "blank run" is first made to determine for a series of pressures at each bomb temperature the effect of pressure and temperature on the apparent volume of the apparatus, including the mercury. The riser-block is thoroughly cleaned and mercury is introduced into the mercury compressor until the end of the capillary leading from the compressor to the riser-block is just filled when the compressor reading is zero. The compressor is then turned back one turn (reading -1) and the capillary connected to the riser-block. A vacuum line is attached to the oil connection of the riser-block.

When the all-steel bomb is used it is evacuated at 400° C, the gold washer closed, the bomb placed in a thermostat at 30 °C, and the bomb capillary attached to the riser-block. The bomb capillary, compressor capillary and riser-block are evacuated and mercury run out of the compressor until it fills the apparatus up to the gold washer and makes contact with the tip of the insulated needle in the riser-block. The vacuum line is disconnected, oil put into the top of the riser-block, and the pressure gauge connected. A series of settings of the compressor for pressures from 5 to 20 atmospheres is made; the gold washer broken by the application of several hundred atmospheres pressure, the bomb filled with mercury, and another series made of settings of the compressor for pressures from 5 to 20 atmospheres. The compressor reading for 30° C and 1 atmosphere (obtained by extrapolation from 5 to 1 atmospheres), corresponding to the volume up to the gold washer, is called the "zero-set"; and the reading for 30° C and 1 atmosphere, corresponding to the volume including that

of the bomb, is called the "bench volume." The difference is the volume of the bomb at 30° C and 1 atmosphere. In some of the measurements the zero-set and bench volume were made at 5 atmospheres instead of being extrapolated to 1 atmosphere; the difference is the volume of the bomb at 30° C and 5 atmospheres, which is below any pressure used in the subsequent compressibility runs.

At each temperature at which gas compressibility data are subsequently to be taken, the compressor readings corresponding to equilibrium are determined for the series of pressures 7, 13, 19, 37, 50, 170, 290, 410, 530, 410, 290, . . . 7 atmospheres. At each pressure one hour is allowed for equilibrium although in general no change is noted after one-half hour. The compressor readings in the increasing pressure series are usually less than those in the decreasing series, the greatest difference being 0.01 turn, or 0.007 cc. The average of the two values is used in the subsequent work, the compressor reading being converted to cubic centimeters of mercury by means of Eq. (7). The result is the apparent volume of the entire system at the given temperature and pressure.

The difference ΔV between the bench volume V_{bench} and the apparent volume $V_{p,t}$ of the entire system when the bomb is at $t°$ C and p atmosphere is expressed by the relation:

$$\Delta V = V_{bench} - V_{p,t} = -(a + bt)\, p + (ct - a) + \Delta_t + \Delta_p, \quad (8)$$

where a, b, c, and d are positive constants, Δ_t a deviation which depends only on temperature, and Δ_p the deviation of the observed ΔV from that calculated by the first three terms of the equation. It was found that the plots of Δ_p against pressure were identical within the experimental error (0.007 cc.) at all temperatures, dropping from + 0.008 cc. at 10 atmospheres to zero at and above 50 atmospheres. Thus the reading of the mercury compressor when the bomb completely filled with mercury is at $t°$ C and p atmospheres is given by the relation:

$$V_{p,t} = V_{bench} - \Delta V. \quad (9)$$

The difference between the bench volume and the zero-set is checked by weighing the amount of mercury in the bomb and capillary up to the gold washer. After the removal of the mercury the bomb is ready for loading with the substance whose compressibility is to be studied. If for any reason the bomb is opened, a new zero-set and bench volume must be determined, since the volume may be changed, but this slight change in volume is not great enough to effect the blank compressibility run.

When the glass-lined bomb is used, the method of procedure is similar. The steel case and the liner are each evacuated at 400° C, the liner sealed off, and enclosed in the case. The zero-set is made with the bomb on its side, the mercury filling the case around the liner. The bomb is set upright whereby the glass tip of the liner is broken and the bench volume is determined. Both the zero-set and the bench volume are extrapolated to zero pressure, the difference being the inside volume of the glass liner at 30° C and zero pressure. This volume is checked by weighing the mercury in the liner, correction being applied for the stretch due to the head of mercury.

4. The Compressibility Measurements.

It is desired to measure the compressibility of a substance along isometrics as well as isotherms. This requires setting the mercury compressor at the correct reading to give the same set of gas densities in the bomb at each temperature.

After the bomb has been evacuated at 400° C and loaded with the substance under investigation, it is connected to the riser-block, the leads evacuated, and a zero-set made. This zero-set will not coincide exactly with that previously measured, due to the difficulty of loading exactly the same amount of mercury into the compressor as in the blank run. The zero-set plus the volume of the bomb gives the new bench volume, V_{bench}.

When the glass-lined bomb is used the zero-set is extrapolated or interpolated to the vapor pressure of the substance at 30° C. A slight correction, determined from the blank run at 30°, is applied for the compressibility of the apparatus between 0 atmospheres and the vapor pressure. The new bench volume is then the new zero-set plus the inside volume of the glass liner.

The only difference between the blank run and the compressibility run is that a certain volume of mercury has been removed from the bomb at $t°$ and introduced into the mercury compressor at 30°. The calculations require a knowledge of the thermal expansion of mercury, and gas volumes at a given temperature are expressed in terms of the volume of mercury at 1 atmosphere and the temperature in question. The density of mercury at 0° C is taken to be 13.5955 grams per milliliter and the variation of volume with temperature at 1 atmosphere pressure is given by Eq. (11), below.

Let m be the number of grams (moles) of substance in the bomb, and let v be the desired specific (molal) volume at $t°$ C and p atmospheres. Then the correct setting C of the mercury compressor is

$$V_{p,t} = aC + \delta C = V_{bench} - mv\frac{d_t}{d_{30}} - \Delta V - D_1 + D_2 + D_3, \quad (10)$$

where:

1. V_{bench} is the bench volume for the compressibility run obtained by adding the volume of the bomb previously determined in the blank run to the zero-set for the compressibility run.

2. mv is the total gas volume, *i. e.* the volume of mercury at $t°$ C which must be withdrawn from the bomb, and d_t and d_{30} are, respectively, the densities of mercury at $t°$ and 30° C and one atmosphere. Since all mercury withdrawn from the bomb is measured at 30° C, the volume of mercury which must be withdrawn into the mercury compressor is mvd_t/d_{30} (subject to the corrections given below).

The density d_t of mercury at one atmosphere is obtained from the formula:[11]

$$V_t = V_o \{ 1 + 10^{-6} (181.456\, t + 0.009205\, t^2 + 0.000006608\, t^3 + 0.000000067320\, t^4) \}, \quad (11)$$

where V_t is the specific volume at $t°$ C and V_o that at 0° C.

3. ΔV is the correction determined in the blank run for the effect of the bomb temperature t and the pressure p on the setting of the mercury compressor. It is read from plots or given by Eq. (8).

4. D_1 is the correction for the change of the compressibility of mercury with temperature and for the compressibility of the steel piston withdrawn. During the compressibility run a certain volume of mercury (approximately mv), which was at $t°$ in the blank run, has been withdrawn into the mercury compressor at 30°, also the same volume of steel piston has been withdrawn from the compressor. The temperature coefficient of the compressibility of mercury[12] $\left(\frac{1}{V}\frac{\partial}{\partial T}\frac{\partial V}{\partial p}\right)$ is 5.5×10^{-9} per atmosphere-degree C and the coefficient of compressibility of steel $\left(\frac{1}{V}\frac{\partial V}{\partial p}\right)$ is 5.8×10^{-7} per atmosphere. Hence

$$D_1 = \{5.8 \times 10^{-7} + 5.5 \times 10^{-9} (t - 30)\} (p - 1)\, mv. \quad (12)$$

It will be noticed that at constant temperature D_1 does not vary greatly with pressure, since the pressure-volume product for a given mass of gas does not change greatly.

[11] International Critical Tables, Vol. II, p. 457. New York: McGraw-Hill Book Co., Inc., 1927.

[12] L. B. Smith and F. G. Keyes, Proc. Am. Acad. Arts and Sci., **69**, 313 (1934).

5. D_2 corrects for the volume of liquid mercury lost by evaporation into the gas space:

$$D_2 = \frac{200.6\ p_{Hg} mv}{RTd_t}, \tag{13}$$

where p_{Hg} is the vapor pressure of mercury at $T°$ K and under the total pressure p. This correction is negligible for temperatures below 200° C.

6. D_3 is the correction for the variation with temperature of the volume (2.4 cc.) of mercury in the riser-block, bomb stopcock, and the capillaries at room temperature.

The three corrections, D_1, D_2, D_3, are all very small and can easily be made with a total uncertainty of 0.001 cc. or less.

The calculated volume $V_{p,t}$ can then be translated into a compressor setting which gives the readings for the desired volume. The corrections 3 and 4 depend on the pressure, which at the start of a measurement is unknown. The pressure is estimated and a provisional compressor setting computed. The pressure is then measured and a new setting computed. Since ΔV varies slowly with pressure, and D_1 is very small the calculations converge rapidly, two computations usually being sufficient to obtain the compressor setting to 0.001 turn.

The pressure p_{Gas} exerted by the gas is given by the relation:

$$p_{Gas} = p + p_{Bar} + p_{Level} + p_{Meniscus} - p_{Hg}, \tag{14}$$

where:

1. p is the pressure measured on the dead-weight gauge.
2. p_{Bar} is the corrected barometric pressure.
3. p_{Level} is the correction for the differences in oil-levels and mercury-levels, reduced to normal atmospheres. The oil head is very small and no correction for the effect of temperature and pressure is applied. The mercury head is divided into two sections, one at room temperature, and one at the thermostat temperature, the dividing line being the outer surface of the thermostat top. The mercury level inside of the all-steel bomb is calculated from the sectional area of the bomb; that for the glass liner determined by running out portions of mercury, weighing them, and measuring the distance from the mercury surface to the top of the outside surface. The results were expressed in plots of the distance from the top surface of the steel bomb (or steel-case) to the mercury surface inside of the bomb against the gas volume mv.

4. $p_{Meniscus}$ is a correction of 1 mm. for the capillary depression at the oil-mercury surface in the riser-block.

5. p_{Hg} is the vapor pressure of mercury corrected for the effect of pressure by the relation:

$$2.303\, RT \log_{10} \frac{p_{Hg}}{p_{o_{Hg}}} = V\,(p_{Gas} - p_{o_{Hg}})\,, \tag{15}$$

where $p_{o_{Hg}}$ is the vapor pressure of mercury (from International Critical Tables) and V the molal volume of liquid mercury at $T°$ K.

At each temperature the pressure is measured for the series of increasing densities and these results checked by measuring the pressures for the series of decreasing densities.

5. Accuracy of the Results.

Pressure. The pressure gauge can be calibrated in terms of the vapor pressure of liquid carbon dioxide at 0° C with an accuracy of 0.004%, which is about the precision in the measurement of a given constant pressure. The use of the same gauge constant up to 500 atmospheres may introduce an error of 0.01 to 0.02% at the higher pressures. The method of obtaining the average temperature of the mercury head in the region of large thermal gradient introduces an uncertainty of 0.5 mm. of mercury when the bomb thermostat is at a high temperature. The overall accuracy of the pressure measurement is from 0.01% in the low pressure, room temperature region of the data, to 0.03% in the high pressure, high temperature region.

Temperature. A given constant temperature can be read with a given platinum resistance thermometer with a precision of 0.002° C. The deviations of the readings of a single platinum thermometer from the international platinum resistance thermometer scale (*i. e.* the scale founded on the average of the readings of a large number of platinum thermometers) increase above 100° C to a maximum of 0.01 to 0.02° C at 325° C.

Volume. The largest uncertainties and those most difficult to estimate are in the measurement of volume. The volumes of mercury forced out by the mercury injector at one atmosphere are known to 0.004 cc. The effect of the temperature of the bomb and of pressure on the apparent volume of the entire system up to the insulated needle is determined in the blank run with an uncertainty of 0.007 cc., and the necessary corrections are either well known (as is the thermal expansion of mercury) or are very small (as are the corrections D_1, D_2, and D_3). Yet, due to hysteresis or other effects, we cannot feel sure

of our volumes to better than 0.05% at the higher pressures and temperatures, and quite often the uncertainty is as great as 0.1%.

Mass. There is no difficulty in determining the mass of gas used to 0.2 milligrams.

Total accuracy. The overall uncertainty in the compressibility data obtained by this method increases from 0.03% at the lower pressures and temperatures to 0.1 to 0.2% at the higher pressures and temperatures.